# Analysis of cement fused beads according to ASTM C114-00

CubiX XRF

## Introduction

The ASTM C114–00 norm gives recommendations concerning the maximum deviations of measured results for a selection of important compounds in cement. According to this norm two criteria apply, one for the differences between duplicates and one for the differences between the averages of the duplicates and the certified values.
To meet this norm a CubiX simultaneous XRF system with fixed channels provides a fast and reliable solution.

## Instrumentation

A PANalytical CubiX simultaneous XRF spectrometer was used. The X-ray source of this system is a 200 W Cr target transmission tube that operates at a fixed setting of 50 kV and 4 mA. The design of this tube allows a very close coupling to the sample. All elements were measured with fixed channels except for Mn, Sr, Ti and Zn which were measured on a programmable goniometer. The norm (excluding Sr) is met within a minimal total measuring time of about 100 s. The measurement time depends on the dilution.

## Sample preparation

To prepare the bead samples the following recipe (dilution: 1:5) was used:

| | | |
|---|---|---|
| Sample | (g) | 1.6 |
| Flux | (g) | 8 (Li-tetraborate - Li-Metaborate 66:34) |
| Oxidizer | (g) | 1 (Ammoniumnitrate (solid)) |
| Oxidization | | 550 °C, 3 min |
| Fusion | | 1120 °C, 6.30 min |

The fusion was carried out on a Perl'X 3 system. The samples thus obtained were 40 mm in diameter.

## Procedure

Eight international SRM-cement standards were selected to produce 2 sets of samples. These sets were used to set up calibrations on the CubiX XRF for the C114 test. Line overlap and matrix corrections were applied where necessary. The results for the differences between duplicates and the average of the duplicates from the certificate are shown in Table 1. Table 2 shows additionally a reproducibility test over 5 days on one sample. This sample was the NIST 1880a.

## Application

The performance of the PANalytical CubiX XRF spectrometer meets the recommendations of the ASTM C114-00 norm for the analysis of cement materials. The samples were prepared as fused beads.

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## Results

| Compound | Certified values NIST 1880A | Difference between duplicates on Day 1 and 2 | Difference allowed (C114-00) | Average concentration of duplicates Day 1 and 2 | Difference measured from certified values | Difference allowed (C114-00) |
|---|---|---|---|---|---|---|
| CaO | 63.8 | 0.05 | 0.2 | 63.8 | 0.01 | 0.3 |
| $SiO_2$ | 20.3 | 0.02 | 0.16 | 20.4 | 0.1 | 0.2 |
| $Al_2O_3$ | 5.2 | 0.00 | 0.2 | 5.2 | 0.05 | 0.2 |
| SO3 | 3.3 | 0.02 | 0.1 | 3.2 | 0.02 | 0.1 |
| $Fe_2O_3$ | 2.8 | 0.001 | 0.1 | 2.8 | 0.02 | 0.1 |
| MgO | 1.7 | 0.00 | 0.16 | 1.9 | 0.16 | 0.2 |
| $K_2O$ | 0.9 | 0.004 | 0.03 | 0.9 | 0.02 | 0.05 |
| $TiO_2$ | 0.3 | 0.003 | 0.02 | 0.3 | 0.01 | 0.03 |
| $P_2O_5$ | 0.2 | 0.002 | 0.03 | 0.2 | 0.01 | 0.03 |
| $Na_2O$ | 0.2 | 0.02 | 0.03 | 0.2 | 0.03 | 0.05 |
| $Mn_2O_3$ | 0.1 | 0.002 | 0.03 | 0.1 | 0.01 | 0.03 |
| SrO | 0.1 | 0.001 | - | 0.1 | 0.01 | - |
| ZnO | 0.005 | 0.000 | 0.03 | 0.01 | 0.01 | 0.03 |
| Cl | 0.004 | 0.003 | 0.02 | 0.00 | 0.001 | - |

*Table 1. Results of duplicates compared with the criteria of the ASTM C114-00. Note: These values include the sample preparation error.*

## Conclusion

The CubiX XRF simultaneous wavelength dispersive X-ray spectrometer provides a fast and reliable solution to analyze cement according to the ASTM C114-00 norm. The accuracy of the calibration is clearly shown by comparing the obtained results with the certified values. The reproducibility is impressively demonstrated when carrying out a repeated measurement.

Note: The RMS for a particular measurement (RMS absolute) can be estimated from:

$$\mathbf{RMS_{(abs)} = K(C + C_0)^{0.5}}$$

where C is in wt%.

**RMS**: **R**oot of the **M**ean **S**quare (=Standard Deviation StDev). Compared to the K-factor (see below), the RMS value does not account for the quality of the standard samples used.

K-value: An additional quality factor that can be considered as a weighted standard deviation. Besides the quality of the analysis, it also reflects the quality of the standards materials used. A lower value indicates a better calibration.

$$K = \sqrt{\frac{1}{n-k}\sum\frac{(C_{Chem} - C_{Calc})^2}{C_{Chem} + C_0}}$$

*Where:*

$C_{Chem}$ = *Certified standard concentration*
$C_{Calc}$ = *Calculated standard concentration*
$C_0$ = *Constant ≈ 0.1*
$n$ = *number of standards*
$k$ = *number of constants calculated (e.g. intercept, E slope)*

**LLD** Lower limit of detection. Value obtained as follows:

$$LLD = \frac{3}{s}\sqrt{\frac{r_b}{t_b}}$$

*Where:*

$r_b$ = *Background countrate (cps)*
$t_b$ = *Counting time background (s)*
$s$ = *Sensitivity (cps)*

| Compound | Certified values NIST 1880A | Diff. between repeated measurements (time interval 5 days) | Difference allowed (C114-00) | Average concentration (time interval 5 days) | Difference measured from certified values | Difference allowed (C114-00) |
|---|---|---|---|---|---|---|
| CaO | 63.8 | 0.004 | 0.2 | 63.8 | 0.01 | 0.3 |
| $SiO_3$ | 20.3 | 0.03 | 0.16 | 20.4 | 0.07 | 0.2 |
| $A_2O_3$ | 5.2 | 0.07 | 0.2 | 5.2 | 0.02 | 0.2 |
| SO3 | 3.3 | 0.00 | 0.1 | 3.2 | 0.01 | 0.1 |
| $Fe_2O_3$ | 2.8 | 0.01 | 0.1 | 2.8 | 0.03 | 0.1 |
| MgO | 1.7 | 0.10 | 0.16 | 1.8 | 0.11 | 0.2 |
| $K_2O$ | 0.9 | 0.008 | 0.03 | 0.9 | 0.02 | 0.05 |
| $TiO_3$ | 0.3 | 0.00 | 0.02 | 0.3 | 0.01 | 0.03 |
| $P_2O_5$ | 0.2 | 0.003 | 0.03 | 0.2 | 0.010 | 0.03 |
| $Na_2O$ | 0.2 | 0.002 | 0.03 | 0.2 | 0.009 | 0.05 |
| $Mn_2O_3$ | 0.1 | 0.02 | 0.03 | 0.1 | 0.002 | 0.03 |
| SrO | 0.1 | 0.001 | - | 0.1 | 0.01 | - |
| ZnO | 0.005 | 0.001 | 0.03 | 0.01 | 0.01 | 0.03 |
| Cl | 0.004 | 0.002 | 0.02 | 0.004 | 0.000 | - |

*Table 2. Results of the reproducibility test. Two repeated measurements with a time span of 5 days.*

| Compound | Concentration range (wt %) | K-value | Typical LLD (ppm, 100 sec) |
|---|---|---|---|
| CaO | 62 - 67 | 0.03 | n.a |
| $SiO_2$ | 20 - 23 | 0.04 | n.a. |
| $Al_2O_3$ | 3 - 6 | 0.01 | 27 |
| SO3 | 2 - 5 | 0.01 | 38 |
| $Fe_2O_3$ | 0.3 - 3.3 | 0.01 | 5 |
| MgO | 0.7 - 2 | 0.03 | 240 |
| $K_2O$ | 0.2 - 1.3 | 0.01 | 6 |
| $TiO_2$ | 0.2 - 0.3 | 0.01 | 2 |
| $P_2O_5$ | 0.03 - 0.2 | 0.03 | 17 |
| $Na_2O$ | 0.02 - 0.19 | 0.02 | 190 |
| $Mn_2O_3$ | 0.03 - 0.3 | 0.02 | 30 |
| SrO | 0.05 - 0.2 | 0.01 | 4 |
| ZnO | 0.01 - 0.03 | 0.02 | 4 |
| Cl | 0.002 - 0.02 | - | 15 |

*Table 3. Calibration data for NIST 188X series. LLD: typical values for lower limit of detection at 100s (obtained from formula listed on page 2). Sample prepared as fused beads. "n.a." stands for "not applicable".*
** The LLD for Mn is higher because of interference with the tube anode element Cr.*

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